

Optically Movable Probes for Surface Enhanced Raman Spectroscopy

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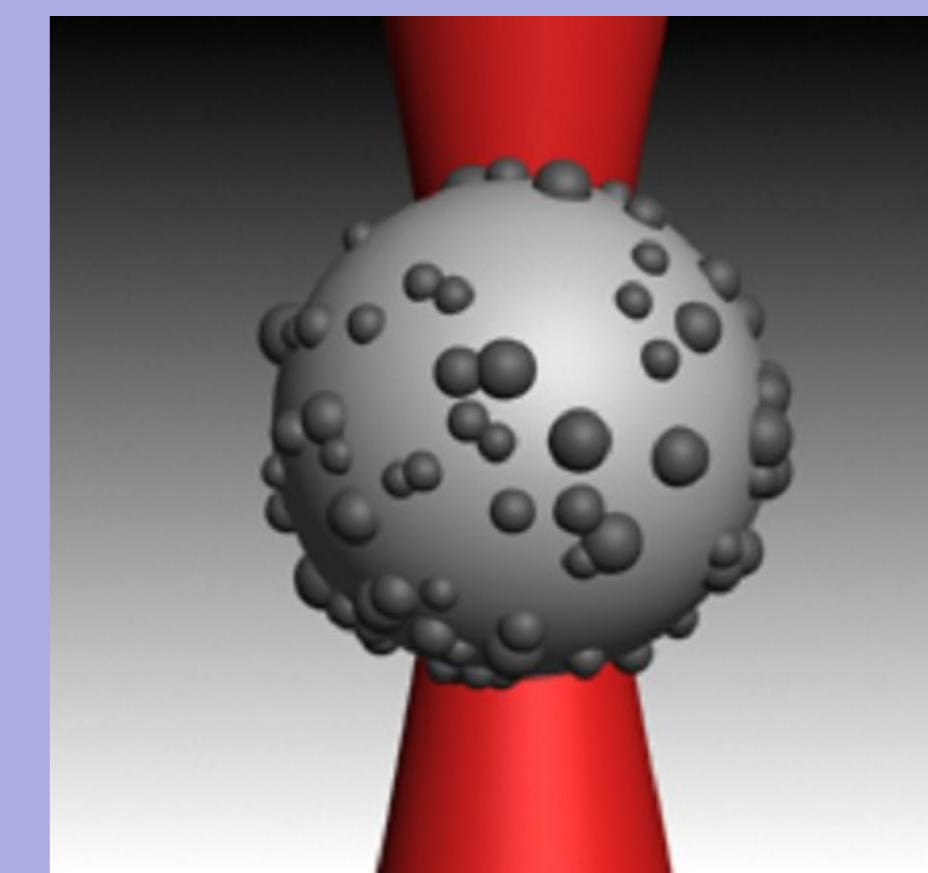
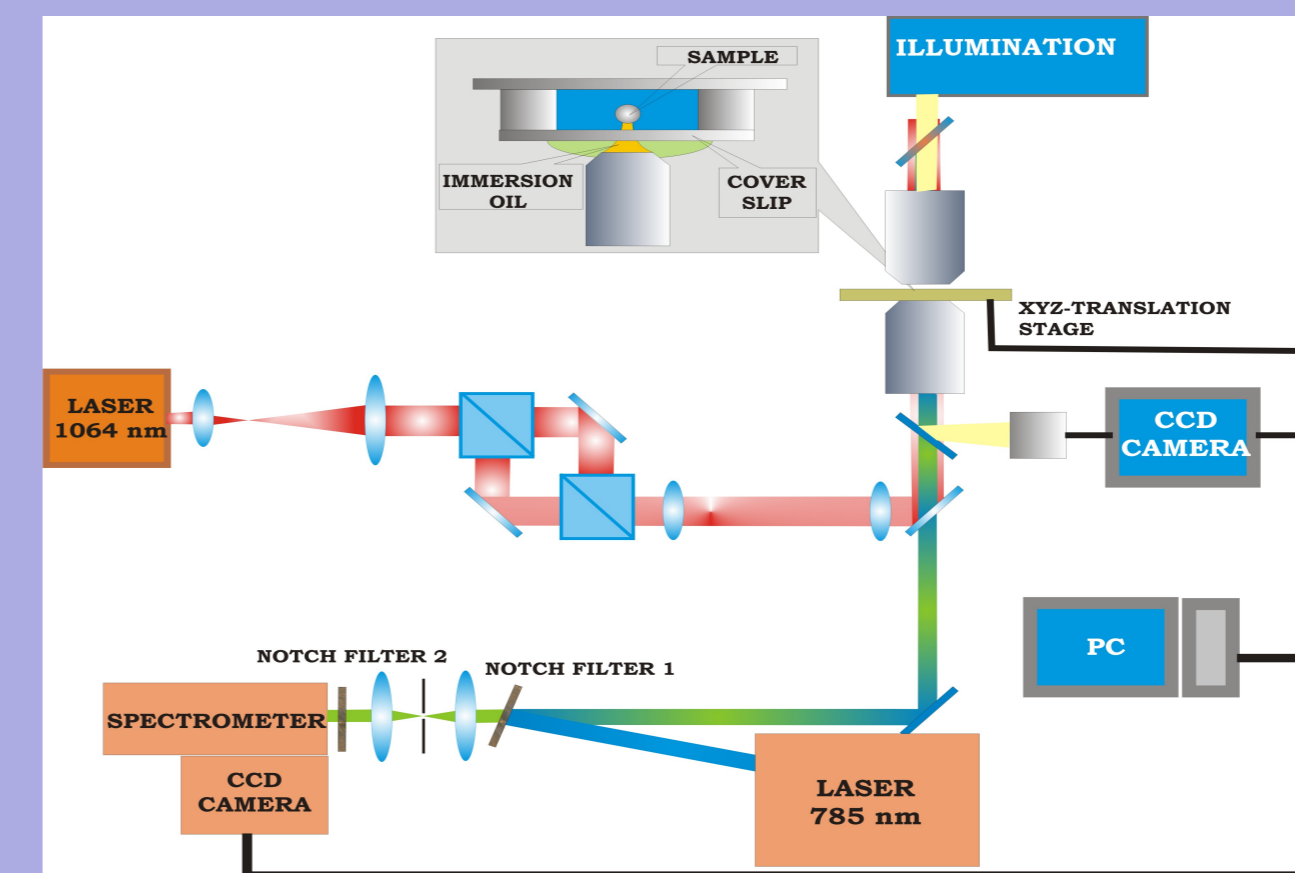
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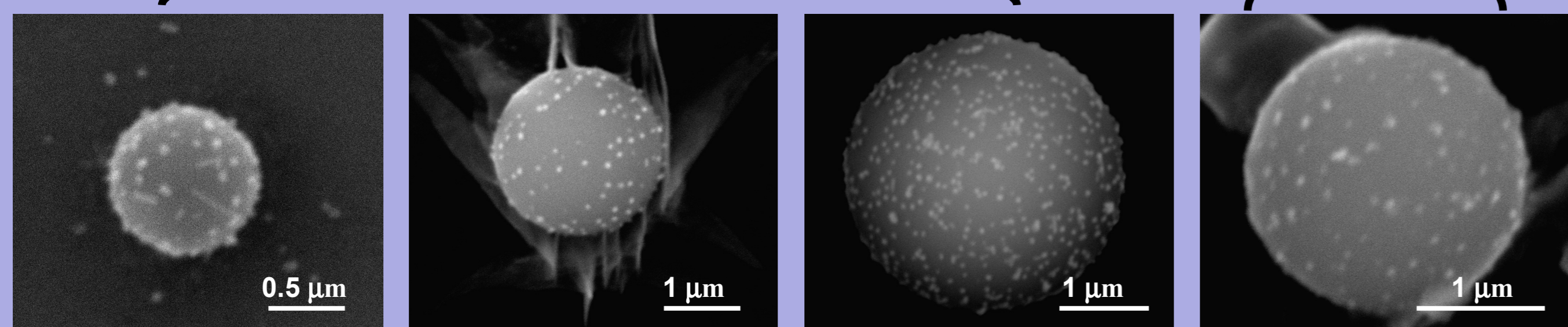
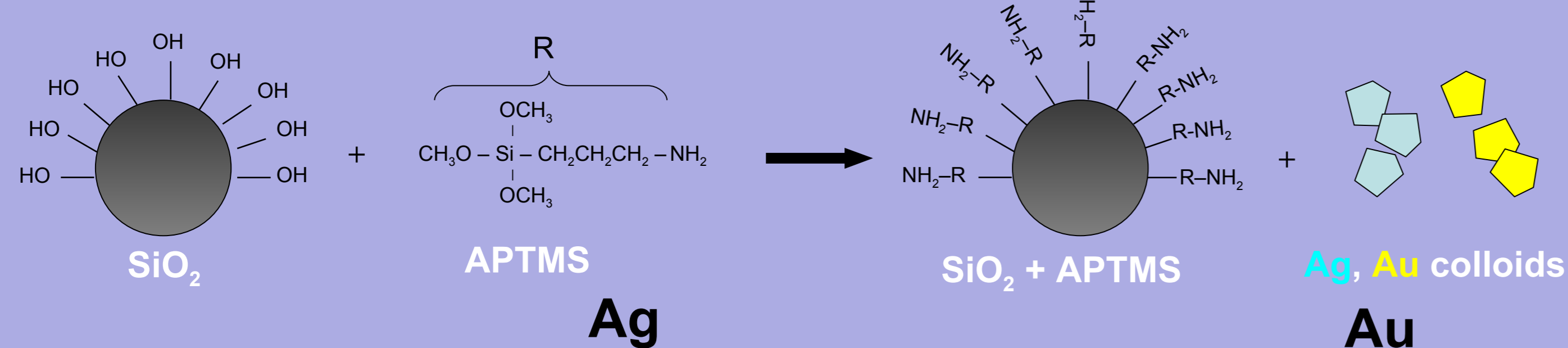
Motivation: To synthesize optically trappable probes that can enhance Raman and luminescence signals through excitation of local plasmons. The probes are intended for the use of chemical analysis in solutions and probing biological systems to detect low concentration of specimens.

Optical setup: A single 785 nm low power (< 10 mW) laser beam passes through a high NA, 100x immersion oil objective, and optically traps the metal covered probe while simultaneously exciting the Raman scattering. Silver and gold colloid covered beads are used.



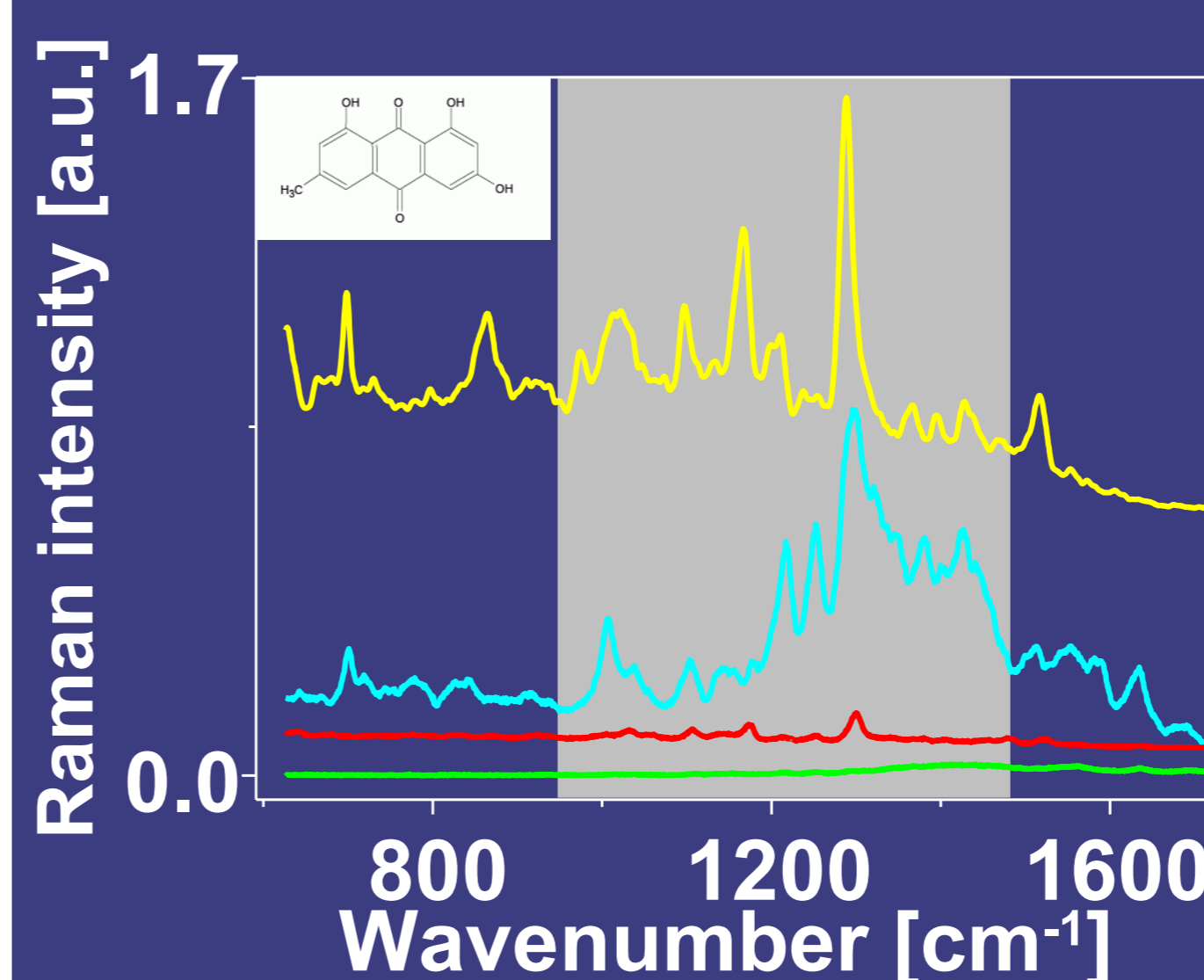
Preparation of dielectric beads partially covered by metal

We attempt to improve the first protocol for producing partially metal covered micron sized beads (McNay, 2004). The method used here is robust and easily reproducible. Silver and gold colloids are prepared by the citrate reduction (Lee-Meisel, Sutherland) method and anchored to the surface of silica beads via a silane monolayer. The diameters of the silver and gold structures are 70 nm and 20 nm (averages), respectively, and silica beads ranging between 1 - 3 μm in diameter are used. A 10% metal coverage on the surface was found to be the optimal value for both trapping and plasmon enhancement. The most critical parameter for colloid attachment to the surface is the agitation speed of the colloid and silane monolayer covered bead solution.

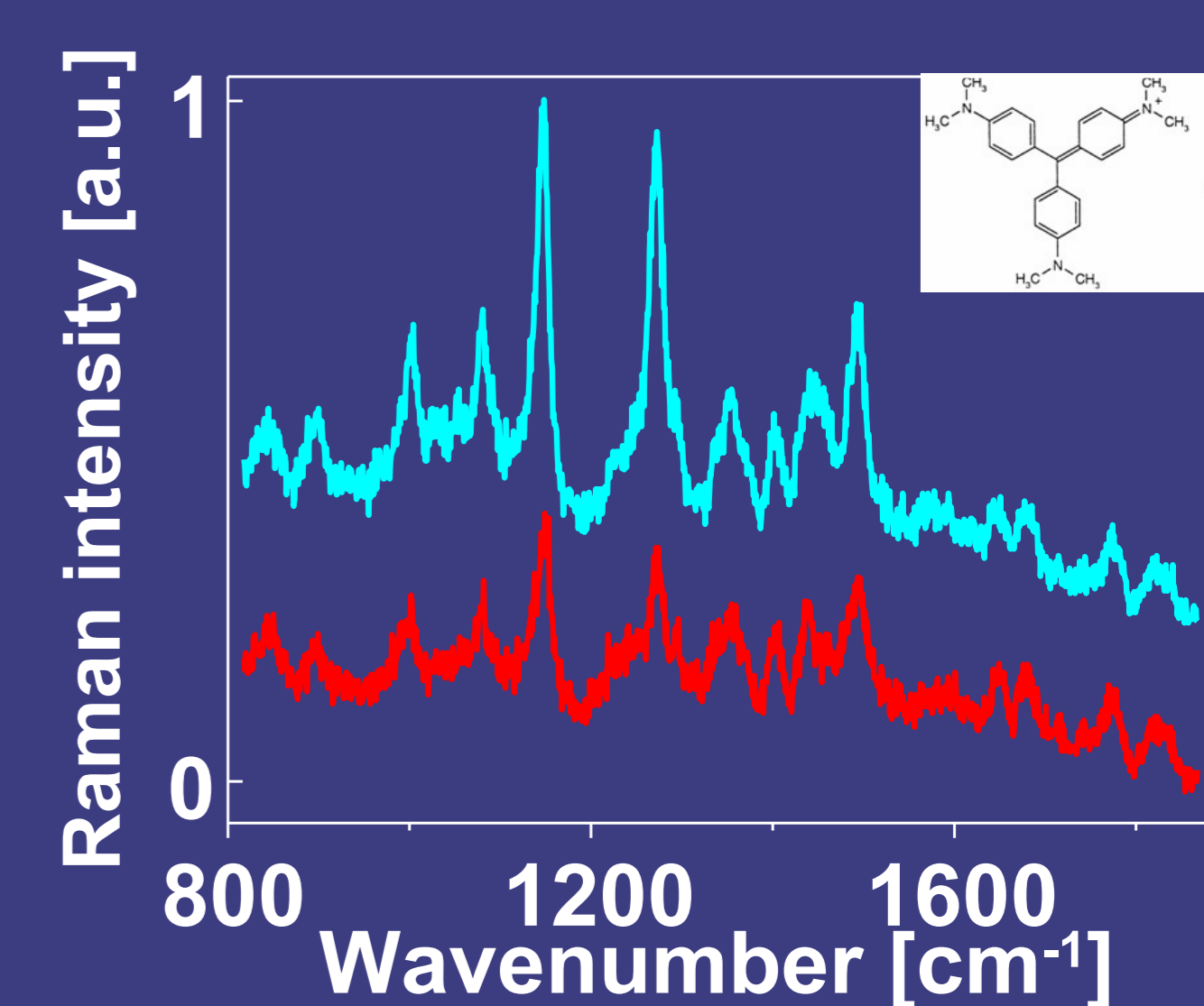


Surface enhanced Raman scattering (SERS)

The metal colloids attached to the surface of the bead are able to enhance the Raman signal of a probe molecule when the bead is trapped. Below are Raman spectra of a silver and gold covered bead in the presence of emodin. A Raman spectrum of a silver coated bead in the presence of crystal violet (CV) is also presented. Strong enhancements of the Raman scattering are observed.



Detection of emodin ($10^{-7}M$) using beads covered by silver and gold colloids

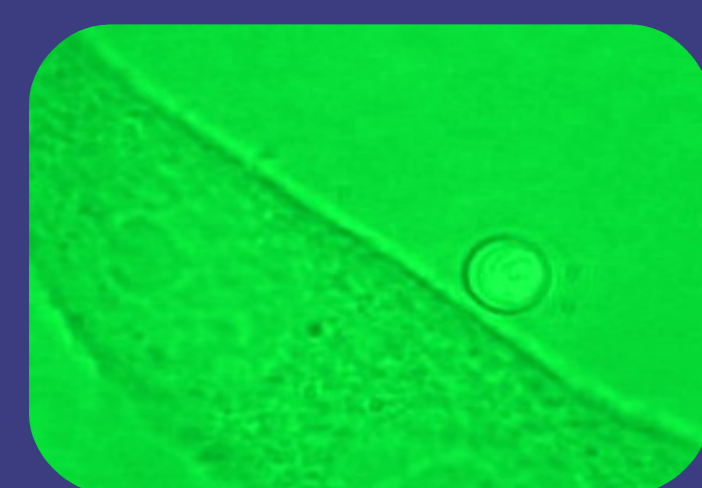


Detection of CV ($10^{-9}M$) using beads covered by silver colloids

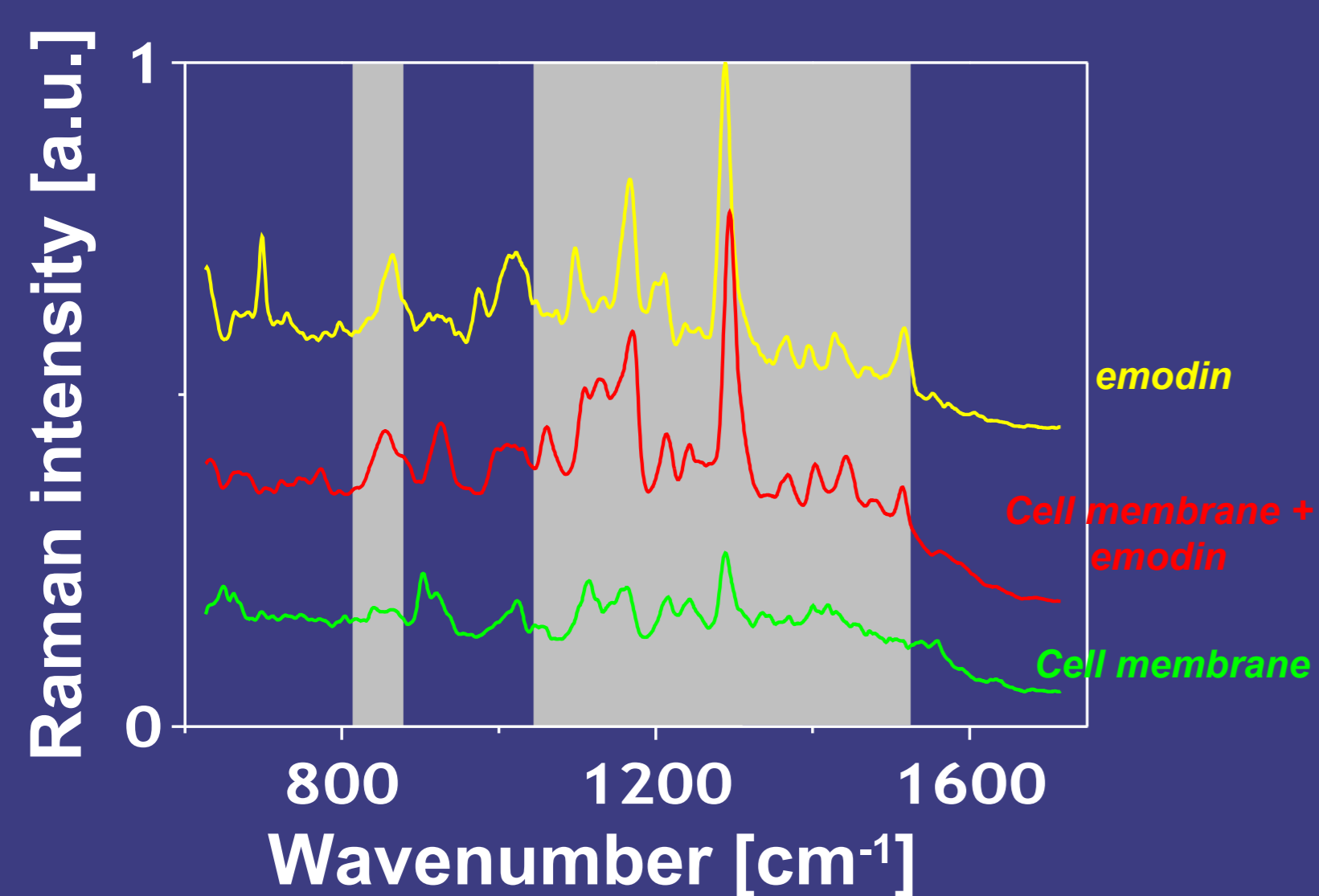
Drug analysis in U-87 MG cell

In order to show the biological application, we attempted to detect the presence of emodin in the membrane of a human glioma cancer cell. We demonstrate two methods:

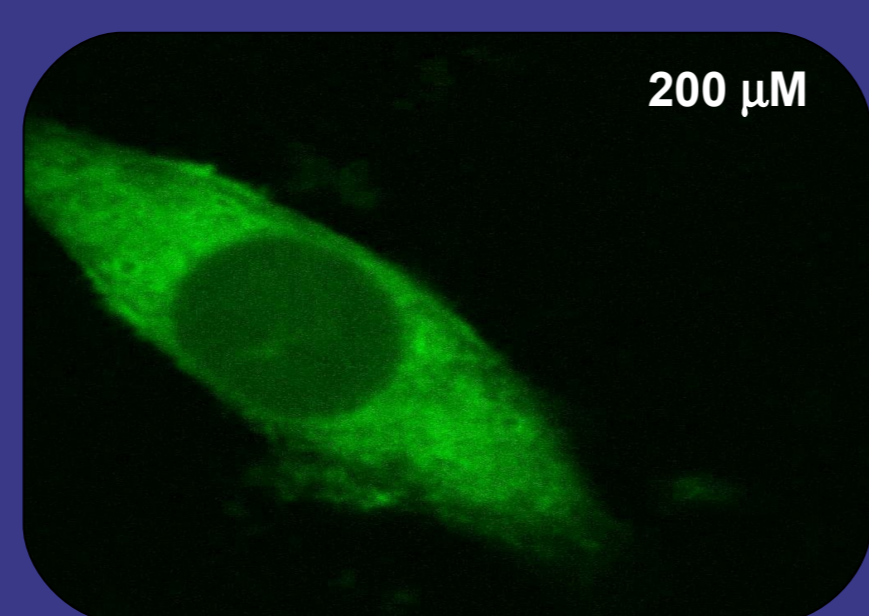
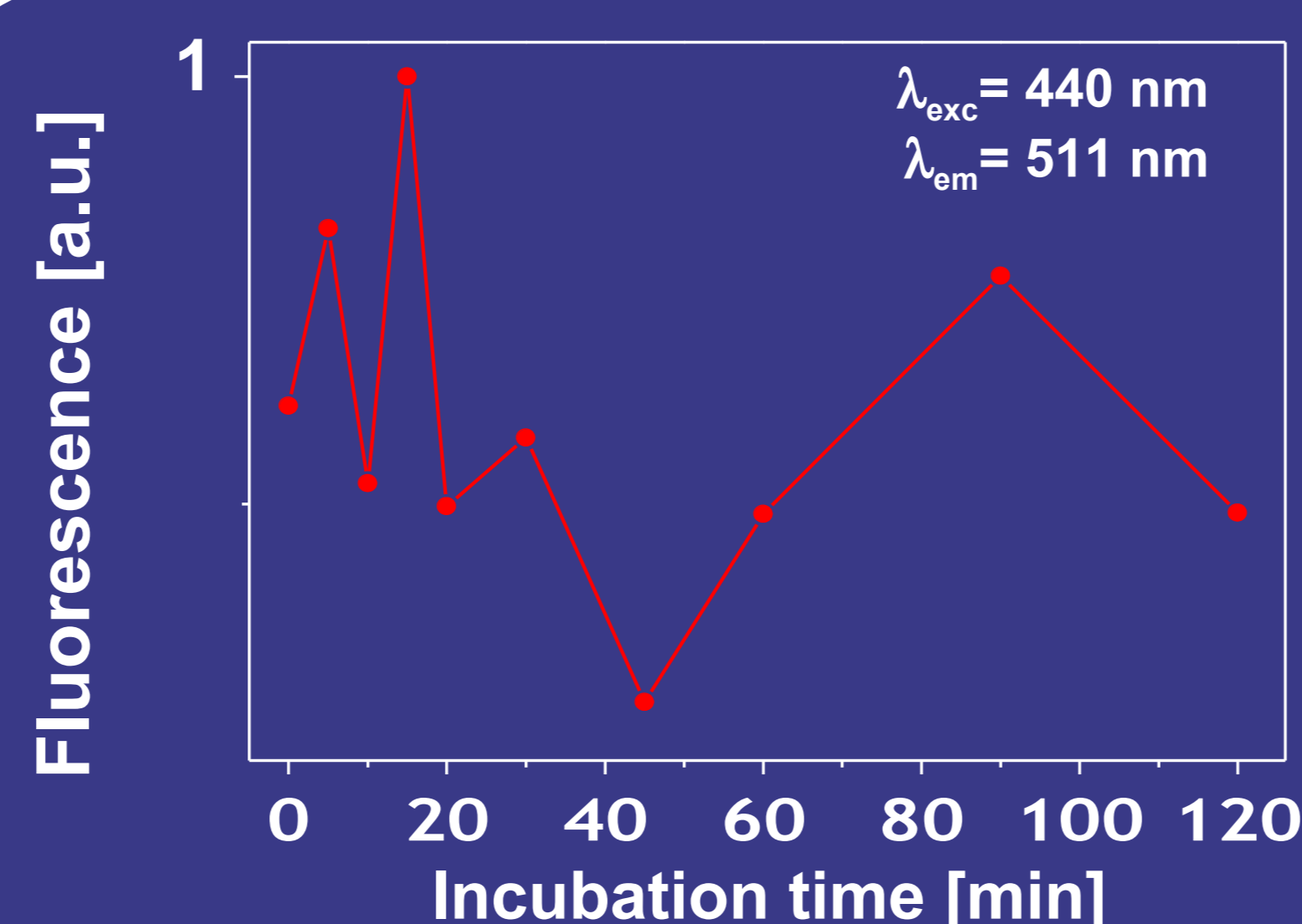
- Drug detection** using a gold covered bead optically trapped and brought in contact with the membrane,
- Drug diffusion monitoring** using a silver covered bead placed inside the cell and compared with fluorescence measurements.



$c = 2 \times 10^{-6} M$



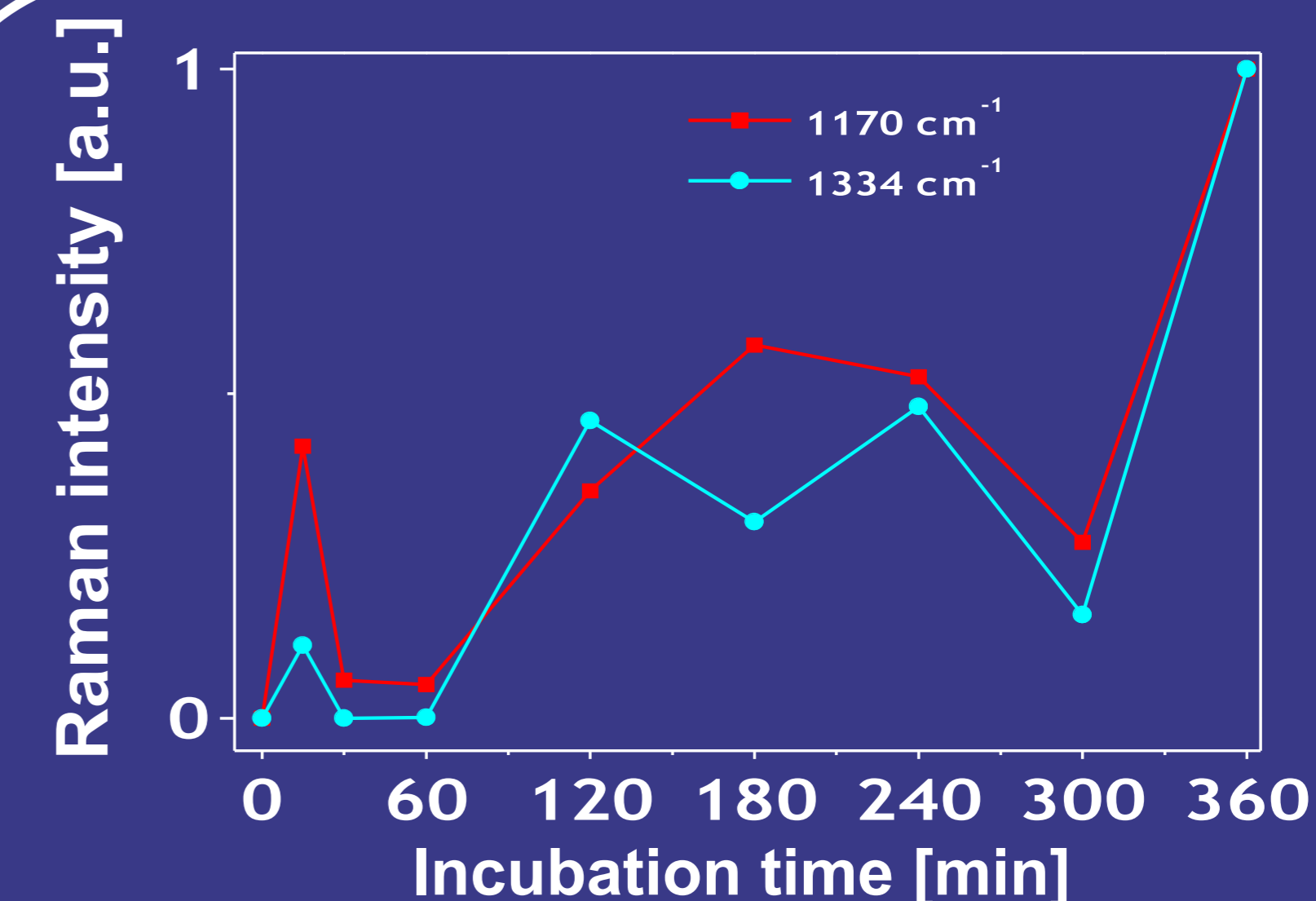
Fluorescence



$c = 20 \times 10^{-6} M$

Monitoring of emodin diffusion ($20 \times 10^{-6}M$) through the U-87 MG cell membrane using fluorescence spectroscopy

SERS



$c = 2 \times 10^{-6} M$

Monitoring of emodin diffusion ($2 \times 10^{-6}M$) through the U-87 MG cell membrane using SERS probes.

Drug diffusion monitoring

Other applications

The probes have been used to study the physical aspects of metal enhanced emission processes by correlating light to optical force. This was achieved by combining photon force microscopy with Raman and fluorescence spectroscopy to study the recoil effects on the trapped bead from the photons emitted through the SERS (Rao, 2009) and SEF (Zhdanov, 2008) phenomena. Our future work utilize the probes for detection, distribution, diffusion and chemical imaging of biologically important molecules and proteins. In addition, these beads will continue to be used in a PFM configuration in order to study other lesser understood optical processes.

We have developed optically trappable Raman enhancing probes. Metal colloids that are known to produce SERS are chemically attached to silica beads at a partial surface coverage. An analysis of the uptake and diffusion of emodin in the U-87 MG cell line was demonstrated using these probes and compared with common fluorescence techniques.

These probes can be manipulated with biological systems *in vivo* therefore opening new possibilities in chemical analysis and cell imaging.

Relevant citations:

- G. McNay, F.T. Doherty, D. Graham, W. Smith, P. Jordan, M. Padgett, J. Leach, G. Sinclair, P. Monaghan, J. Cooper; Visual observation of SERRS from single silver coated silica microparticles within optical tweezers; *Angew. Chem. Int. Ed.*, **43**, 2004, 2512.
- A. Zhdanov, M.P. Kreuzer, S. Rao, A. Fedyanin, P. Ghenuche, R. Quidant, D. Petrov; Detection of plasmon-enhanced luminescence fields from an optically manipulated pair of partially metal covered dielectric spheres; *Optics Letters*, **33**, 2008, 2749.
- S. Rao, Š. Bálint, P. Lovhaugen, M.P. Kreuzer, D. Petrov; Measurements of mechanical forces acting on optically trapped dielectric spheres induced by surface-enhanced Raman scattering; *PRL*, **102**, 2009, 087401.

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